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The Magnetic Properties of $Ni(OH)_2$ and β-$Co(OH)_2$

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The magnetic properties of $Ni(OH)_2$ and β-$Co(OH)_2$ which have cadmium iodide type structure were experimentally studied by measurements of temperature dependence of magnetic susceptibility and magnetic field dependence of magnetization.

In the case of $Ni(OH)_2$, sample, where the c-axis of each particle is oriented in the same direction, was prepared to determine the direction of spin axis.

The results obtained are as the following.

1. At temperatures below 30°K, $Ni(OH)_2$ was antiferromagnetic and the spin axis was directed in parallel to the c-axis. The susceptibility well above the Néel temperature obeyed the Curie-Weiss law with a positive paramagnetic Curie point (35°K). Effective Bohr magneton number was deduced to be 3.2 μ_B. At 4.2°K, the magnetization $M_{//}$, measured when the magntic field was parallel to the c-axis of oriented $Ni(OH)_2$ powder, abruptly increased in the magnetic field about 55 KOe and was saturated by the field above 85 KOe. These phenomena allow to conclude that $Ni(OH)_2$ is metamagnetic; the magnetic moments within a metal ion layer form a ferromagnetic sheet and the moments in adjacent layers are antiparallel, such as in the case of $FeCl_2$.

2. β-$Co(OH)_2$ exhibited an antiferromagnetic behavior below 12.3°K. The susceptibility above 100°K also obeyed the Curie-Weiss law with a positive paramagnetic point (20°K). Effective Bohr magneton number was obtained to be 5.2 μ_B. At 4.2°K, the magnetization gradually increased with increasing magnetic field until it was saturated by the field of about 35 KOe. From these phenomena the metamagnetic behaviors of β-$Co(OH)_2$ were made clear. In this case, it is suggested that the anisotropic field is smaller than the antiferromagnetic internal field and that the spin axis lies in the c-plane.

I. INTRODUCTION

The present paper deals with magnetic properties and magnetic structures of $Ni(OH)_2$ and β-$Co(OH)_2$.

$Ni(OH)_2$ and β-$Co(OH)_2$ have a hexagonal layer structure of CdI_2 type which consists of metal ions seperated by two layers of OH ions.

The anhydrous dichlorides of iron, nickel and cobalt, which also have a $CdCl_2$ type structure, have antiferromagnetic spin structures[1]. In the antiferromagnetic state, the magnetic moments of metal ions within a layer are strongly coupeld ferromagnetically, while the moments in adjacent layers are weakly coupled antiparallel. Because of this characteristic magnetic structure, these chlorides of iron group exhibit an unusual magnetic behavior called "Metamagnetism".

In contrast with an usual antiferromagnet, the magnetic susceptibility at the

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temperature well above the transition point obeys the Curie-Weiss law $\chi=C/T-T_\theta$ with a positive paramagnetic Curie point (T_θ), because the ferromagnetic internal field is stronger than the antiferromagnetic internal field. For magnetization, $FeCl_2$ [2,3] which is antiferromagnetic below T_N(25°K) shows the transition from antiferromagnet to ferromagnet by the application of the external magnetic field of 11 KOe at 4.2°K. This transition was observed by the sudden increase of the magnetization. Magnetizations of $CoCl_2$ [2,3] and $NiCl_2$ [2,3] do not show such a behavior as that of $FeCl_2$ but show the gradual increase with increasing magnetic field.

This phenomenon of "Metamagnetism" was theoretically explained by Kanamori[4].

The anisotropy field H_A of $FeCl_2$, of which the spin axis is parallel to the c-axis, is much larger than the antiferromagnetic internal field H_E. Therefore, when the external field is applied in parallel to the c-axis, antiferromagnetic $FeCl_2$ can directly change to ferromagnetic $FeCl_2$ before the external field reaches the antiferromagenetic critical field $H_C'=\sqrt{2H_AH_E/1-\frac{\chi_{//}}{\chi_\perp}}$.

In the cases of $CoCl_2$ and $NiCl_2$, where spin axis lies in the c-plane and H_A is much smaller than H_E, the spin direction changes to be perpendicular to the magnetic field before the transition from antiferromagnetic to ferromagnetic occurs, when the field is applied in perpendicular to the c-axis. When the magnetic field higher than H_C' is applied, the magnetization increases linearly inclined at $\chi_\perp$ till it is saturated by the field equal to $2H_E$. When magnetic field is applied in parallel to the c-axis, the magnetization increases linearly inclined at $\chi_\perp$ with increasing field. Therefore, the magnetization courves of powder sample of $CoCl_2$ and $NiCl_2$ consist of the mixture of the curves of parallel and perpendicular magnetization.

Considering the crystallographic analogy between hydroxides and anhydrous chlorides of iron group, hydroxides were expected to show a metamagnetic property.

In the present paper, susceptibilities of powder $Ni(OH)_2$ and β-$Co(OH)_2$ were measured from 1.2°K to room temperature and the measurements of susceptibilities parallel and perpendicular to the c-axis were carried out on oriented $Ni(OH)_2$ sample and the determination of the spin axis was attempted.

The magnetizations of these hydroxides were measured up to 90 KOe at 4.2°K to determine whether they are metamagnetic or not.

II. EXPERIMENTALS

1) Preparation of $Ni(OH)_2$ sample

The particles of $Ni(OH)_2$ [5] obtained by adding alkaline solution to nickelous salt solution are very fine (about 100 Å in size). It was inferred that these fine particles would show magnetically the characteristic behaviors such as superparamagnetism and superantiferromagnetism. In order to avoid these size effects, it is necessary that the particle size is larger than about 1 μ.

The sample for the magnetic measurements was prepared as follows;

0.1 M-$Ni(NO_3)_2\cdot 6H_2O$ aqueous solution was mixed with 0.2 M-NH_4OH aqueous

solution and kept stirring at room temperature for 3 hours. The particles of $Ni(OH)_2$ were grown by hydrothermal reaction at 250°K for 7 hours.

This sample was confirmed to be $Ni(OH_2)$ by X-ray diffraction. Each particle of $Ni(OH)_2$ had a thin hexagonal plate-like shape and was $1\sim3\,\mu$ in size as shown in the electron micrograph (Fig. 1 (a)).

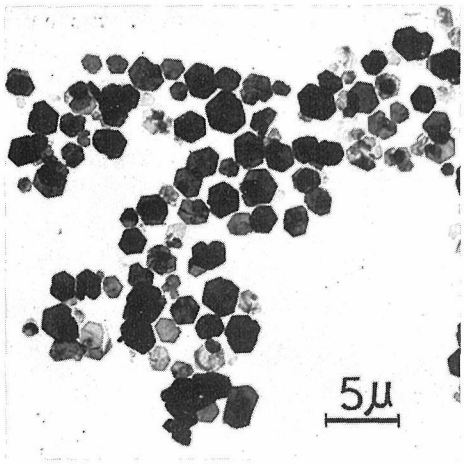

Fig. 1 (a). Electron microphotograph of $Ni(OH)_2$.

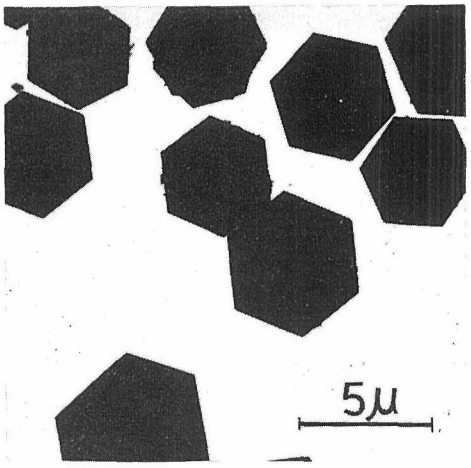

Fig. 1 (b). Electron microphotograph of β-$Co(OH)_2$.

2) Preparation of oriented sample of $Ni(OH)_2$

As shown in Fig. 1 (a), each particle of $Ni(OH)_2$ is thin hexagonal plate-like in shape. Therefore, the particles were preferentially oriented to one direction of the c-axis by sedimentation of particles in water.

When X-ray beams are reflected from the plane parallel to the c-plane of an ideally oriented sample, all (*hkl*) reflections except (*00l*) reflections disappear from X-ray diagram. The X-ray diffraction diagram of oriented $Ni(OH)_2$ particles is shown in Fig. 2. From this diagram each particle was confirmed to be fairly oriented.

3) Preparation of β-$Co(OH)_2$ sample

It was reported by Milligan[6] that there are two modifications, α- and β-form in $Co(OH)_2$. When aqueous solution containing Co^{++} was mixed with alkaline aqueous solution, α-$Co(OH)_2$, which was blue amorphous precipitates, was obtained first but gradually disappeared and β-$Co(OH)_2$ of pink coloured crystalline was precipitated.

The sample for the magnetic measurements was prepared as follows;

0.1M-$CoCl_2\cdot7H_2O$ aqueous solution was mixed with 0.2M-NaOH aqueous solution at 20°C in the atmosphere of nitrogen gas to prevent Co^{++} from oxidation and the mixed solution was reacted for 24 hours. The pink coloured precipitates were confirmed to be β-$Co(OH)_2$ by X-ray diffraction and the average particle size was observed to be several microns as shown in Fig. 1 (b).

4) The magnetic measurements

The magnetic susceptibility was measured by AC Hartshorn bridge method

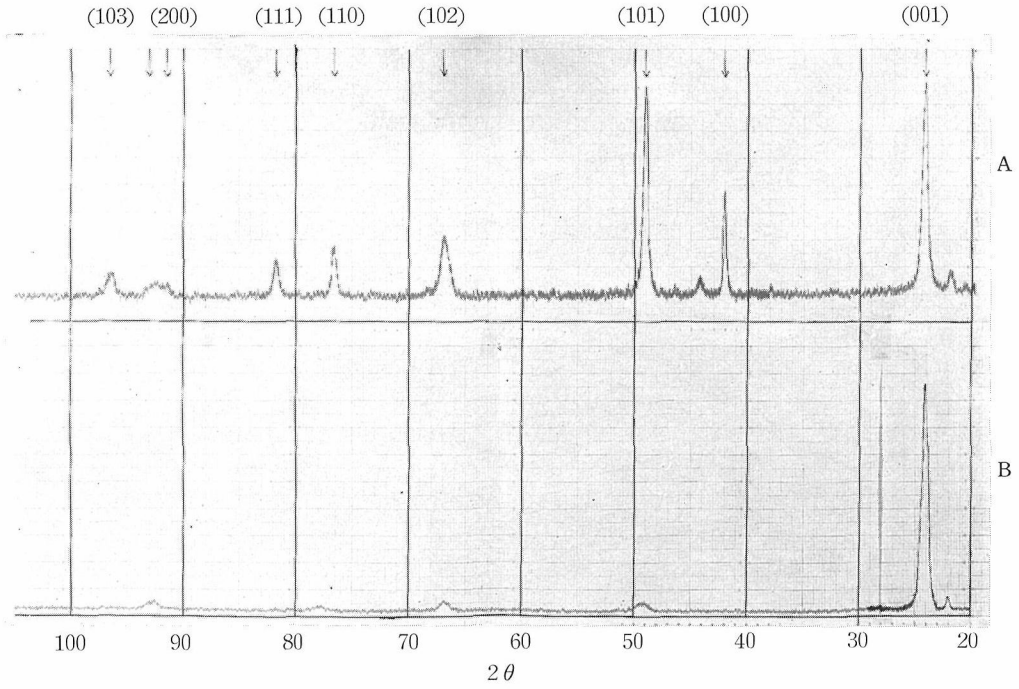

Fig. 2. X-ray diagram of oriented and powder $Ni(OH)_2$.
A : Oriented $Ni(OH)_2$ B : Powder $Ni(OH)_2$

at temperatures from 1.2°K to 90°K and by a magnetic torsion balance from 90°K to room temperature. The temperature from 90°K to room temperature was determined by employment of Au-Co : Cu thermocouple and below 90°K it was determined by measuring the electric resistance of the calibrated Ge resistor.

For the measurements of the magnetization in the magnetic field 90 KOe, two inversly wound search coils with the same coil constants were placed in a magnetizing solenoid. A flux change in search coils due to the displacement of the specimen from one search coil to another was measured by recording flux meter. The temperature was determined by He vapor pressure.

III. RESULTS AND DISCUSSIONS

1) $Ni(OH)_2$

The temperature dependence of χ and χ^{-1} of random oriented powder sample is shown in Fig. 3.

The experimental fact that χ showed a very sharp maximum at 30°K, allows to suppose that the sample is antiferromagnetic below 30°K(T_N). Susceptibilities parallel and perpendicular to the c-axis of oriented sample were measured to determine the spin axis in the antiferromagnetic state. As shown in Fig. 4, $\chi_\perp$, where $\perp$ means to be perpendicular to the c-axis of the oriented $Ni(OH)_2$ sample, had a value of 6.66×10^{-2} emu/mol which was almost independnt of the temperature below T_N. On the other hand, $\chi_{/\!/}$ parallel to the c-axis decreased with decreasing temerature through a prominent maximum value 10.11×10^{-2} emu/

mol at T_N. These results show the spin axis of $Ni(OH)_2$ to be parallel to the c-axis.

As shown in Fig. 3, χ in temperature range from about 150°K to room temperature obeyed Curie-Weiss law with a positive value of T_θ(35°K). Effective Bohr magneton number was 3.2 μ_B, calculated from the equation of $C=N\mu^2_{Beff}/3k$. Beacause of the positive sign of T_θ, it was expected that the ferromagnetic internal field of $Ni(OH)_2$ was larger than the antiferromagnetic internal field and $Ni(OH)_2$ would be a metamagnetic substance.

The magnetization measurements were carried out up to 90 KOe at 4.2°K on the powder sample and the oriented sample, to study whether $Ni(OH)_2$ shows the metamagnetic property. As shown in Fig. 5, the abrupt increase of M_p, magnetization of powder sample, was observed in about 55 KOe. The magnetization parallel to the c-axis of the oriented sample, $M_{//}$, increased more abruptly than M_p in 55 KOe and showed almost all the fraction of saturation magnetization at 90 KOe. Therefore the abrupt increase of M_p and $M_{//}$ observed in about 55 KOe shows to be due to the transition from antiferromagnet to ferromagnet. From these reults, it is apparent that $Ni(OH)_2$ is concluded to be a metamagnetic substance and that the anisotropy field H_A is much stronger than the antiferromagnetic internal field H_E. The magnetization perpendicular to the c-axis, $M_\perp$,

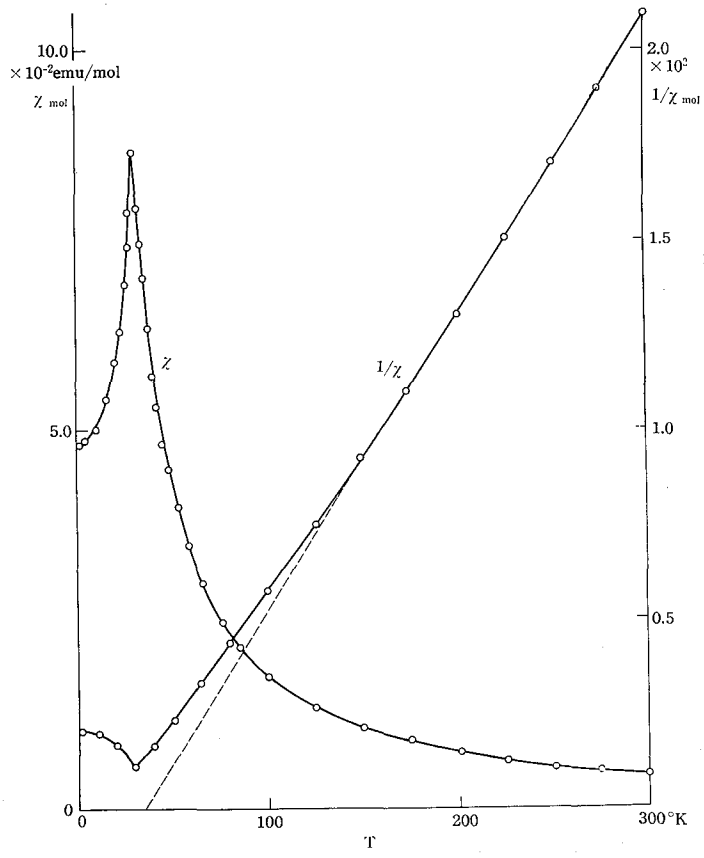

Fig. 3. Temperature dependence of susceptibility of powder $Ni(OH)_2$.

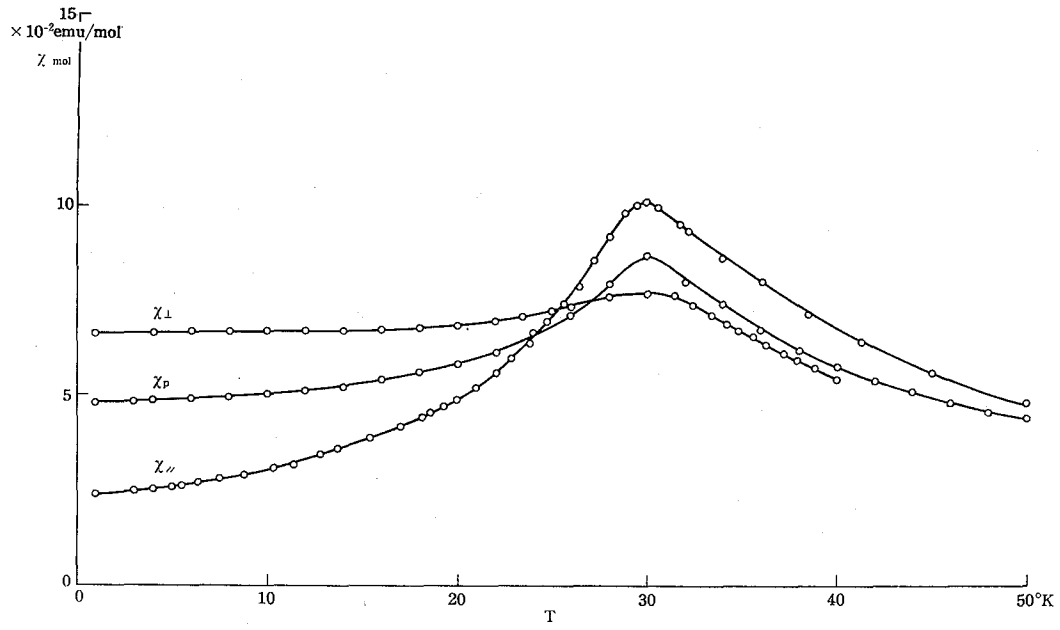

Fig. 4. Temperature dependence of susceptibility of oriented $Ni(OH)_2$.
$\chi_\perp$: Perpendicular to the c-axis of oriented $Ni(OH)_2$.
$\chi_{/\!/}$: Parallel to the c-axis of oriented $Ni(OH)_2$.
χ_p : Susceptibility of powdered $Ni(OH)_2$.

increased almost linearly up to 90 KOe with the increasing field. By extrapolation of the magnetization, $M_\perp$ was expected to be saturated with about 150 KOe.

According to the molecular field theory, $M_\perp$ is saturated by the field which is twice as large as the antiferromagnetic internal field. As the antiferromagnetic internal field is equal to 55 KOe, $M_\perp$ is expected to be saturated by the field about 110 KOe. This difference between the expected value and the experimental one may be due to a large anisotropy concluded above.

2) **β-$Co(OH)_2$**

The temperature dependence of χ and χ^{-1} of powder sample is shown in Fig. 6. The experimental fact χ represented a very sharp maximum when the temperature was 12.3°K, indicates that the sample is antiferromagnetic below 12.3°K. In the temperature range from about 100°K to room temperature χ was observed to obey the Curie-Weiss law with a positive T_θ(20°K). The effective Bohr magneton number was deduced to be 5.2 μ_B.

In order to study the magnetic behavior under the high magnetic field below T_N(12.3°K), the magnetization was measured up to 80 KOe at 4.2°K. As shown in Fig. 7, the magnetization did not show such an abrupt increase as $Ni(OH)_2$ but increased gradually with increasing field and was almost saturated above fields of about 35 KOe. This critical field (35 KOe) is much smaller than those usually associated with the exchange coupling in an antiferromagnetic structure which has the transition temperature of 12.3°K.

The magnetization in the low field, 0~5 KOe, increased in proportion to the

field, in the field ranging from 5 KOe to 22 KOe, increased in rather larger rate than initial susceptibility and in higher field, from 22 KOe to 28 KOe, increased linearly with the field. This magnetization curve is essentially identical to that observed in $CoCl_2$, thereby suggesting H_A is smaller than H_E.

Therefore, the direction of spin axis was inferred to be at random in the low field but in the field range from 22 KOe to 28 KOe, to be perpendicular to the field. In general H_A is much large when the spin axis is parallel to the c-axis. The result that H_A is smaller than H_E suggests the spin axis lies in the c-plane.

IV. CONCLUSION

Powder samples of $Ni(OH)_2$ and β-$Co(OH)_2$ were prepared from aqueous solution and the magnetic properties were studied. In the case of $Ni(OH)_2$, the

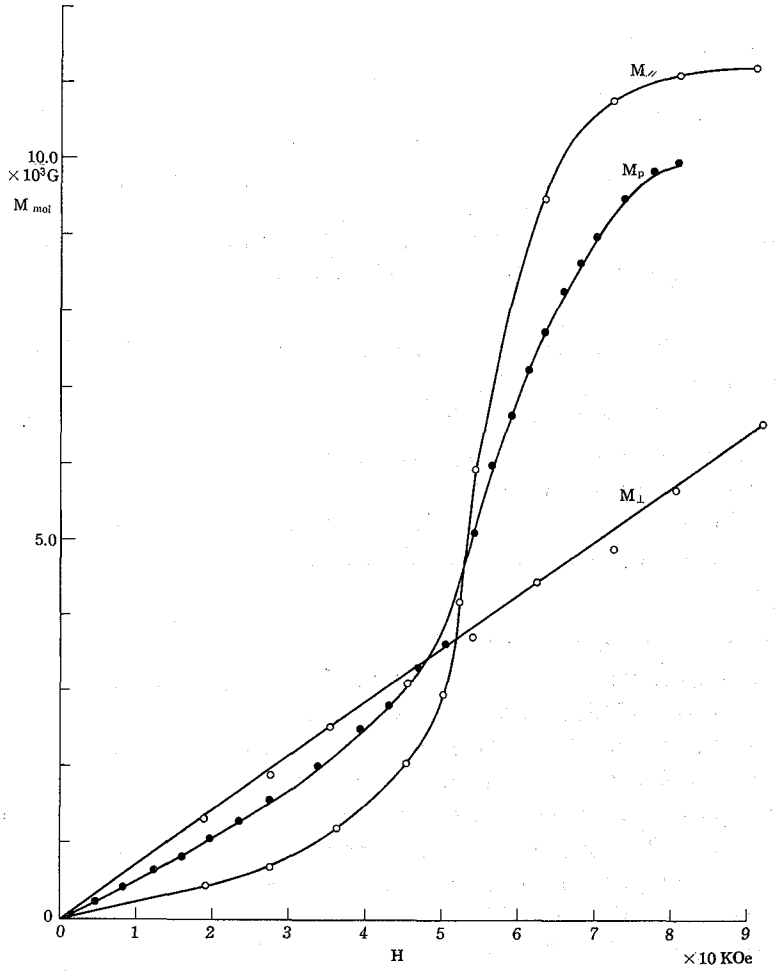

Fig. 5. Magnetic field dependence of magnetization of $Ni(OH)_2$ at 4.2°K.
$M_{//}$: Magetization parallel to the c-axis of $Ni(OH)_2$.
$M_{\perp}$: Magetization perpendicular to the c-axis of $Ni(OH)_2$.
M_p : Magnetization of powder $Ni(OH)_2$.

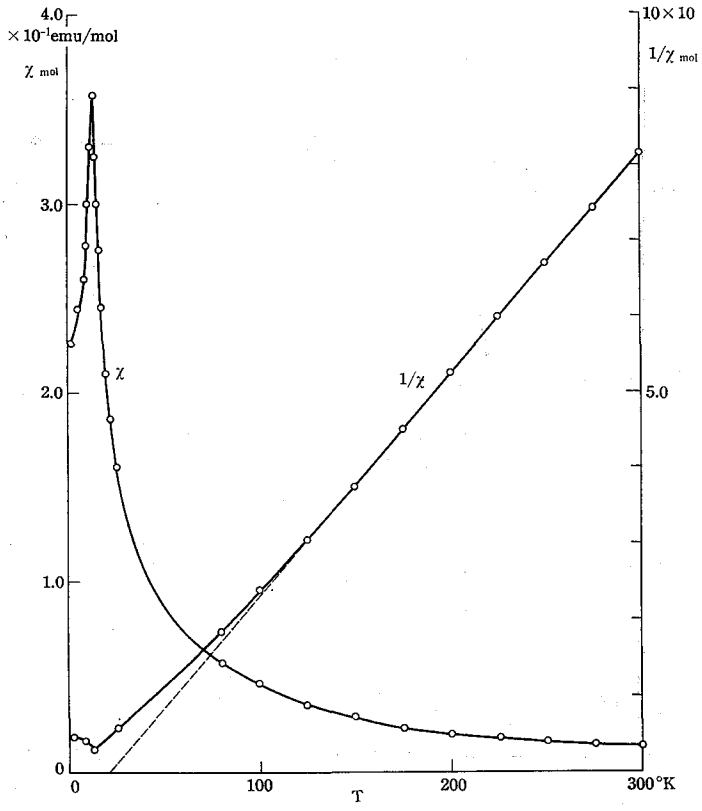

Fig. 6. Temperature dependence of susceptibility of β-$Co(OH)_2$.

magnetic measurements were carried out on oriented samples.

Susceptibility of $Ni(OH)_2$ exhibited an antiferromagnetic temperature dependence with the sharp maximum at 30.0°K. Well above T_N, χ obeyed the Curie-Weiss law and paramagnetic Curie point T_θ was a positive value, 35°K. Below T_N, $\chi_\perp$, perpendicular to the c-axis of oriented $Ni(OH)_2$, was almost constant thereby the spin axis was parallel to the c-axis.

The magnetization parallel to the spin axis of $Ni(OH)_2$ exhibited the abrupt increase in the field of 55 KOe at 4.2°K. This abrupt increase was due to the transition from antiferromagnet to ferromagnet and showed that $Ni(OH)_2$ was the metamagnetic substance, of which H_A was much larger than H_E. Therefore it can be concluded that the magnetic moments of Ni atoms within a layer form a ferromagnetic sheet while the moments in adjacent layers are coupled anti-parallel.

β-$Co(OH)_2$ exhibited a sharp maximum in χ at 12.3°K. The temperature dependence of χ of β-$Co(OH)_2$ was typical one of antiferromagnet except the fact that T_θ was the positive value of 20°K.

The magnetization of β-$Co(OH)_2$ was saturated by the field of about 35 KOe, although the sharp transition such as in the case of $Ni(OH)_2$ did not occur. The magnetization curve of β-$Co(OH)_2$ is essentially similar to that of $CoCl_2$ which

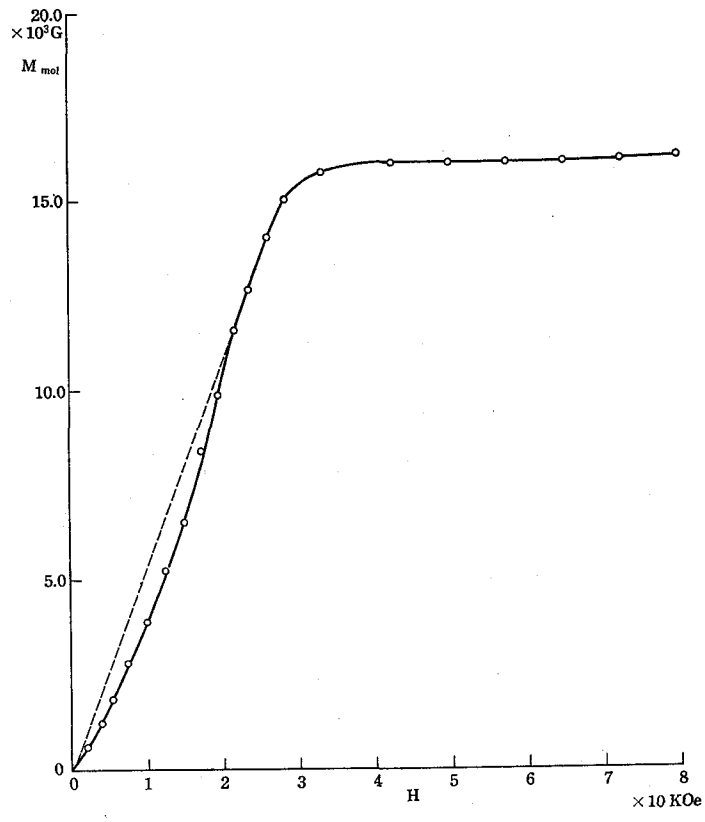

Fig. 7. Magnetization of β-$Co(OH)_2$ at 4.2°K.

has the metamagnetic structure with much smaller H_A than H_E. Therefore the magnetic structure of β-$Co(OH)_2$ was inferred to have analogous magnetic properties of $Ni(OH)_2$ except that the magnetic easy axis lies in the c-plane.

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REFERENCES

(1) M. L. Willkinson and J. W. Cable, *Bull. Amer. Phys. Soc.* 1, 190 (1956).
M. L. Willkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, *Phys. Rev.* 113, 497 (1959).

(2) C. Starr, F. Bitter, aud A. R. Kaufmann, *Phys. Rcv.* **58**, 977 (1940).
(3) H. Bizette, *Compt. Rend.* **243**, 895, 1259 (1956).
(4) J. Kanamori, *Metal Physics* (*in Japanese*) **3**, 104 (1957).
J. Kanamori, *Prog. Theor. Phys.* **20**, 890 (1958).
(5) W. Lotmar and W. Feitknecht, *Z. Krist.* **93A**, 688 (1936).
(6) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.* **36**, 722 (1932).